

AEDC-TR-67-65



INVESTIGATION OF A RAPID-QUENCH SAMPLING PROBE FOR NONEQUILIBRIUM AIR FLOWS

F. J. Stoddard and W. S. Watt

Cornell Aeronautical Laboratory, Inc.

Buffalo, New York

March 1967

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FOREWORD

The work reported herein was sponsored by Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC), Arnold Air Force Station, Tennessee, under Program Element 61405014, Project 8951, Task 895106.

One objective in this program is the development of a gas-sampling probe as a diagnostic tool. Sponsorship is by AEDC under Contract No. AF 40(600)-1093, under the technical cognizance of Captain C. O. Forsythe. This report is an interim report on the gas-sampling probe and covers the period 1 March 1965 through 1 July 1966. The manuscript was submitted for publication on March 21, 1967.

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The authors gratefully acknowledge the aid of Dr. J. Gordon Hall who suggested this study, and the advice of A. Russo, R. J. Vidal, J. Hilton, and R. A. Fluegge on various aspects of this research.

This technical report has been reviewed and is approved.

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ABSTRACT

Shock tunnel experiments in air are reported which basically were designed to determine the free-stream composition from the gaseous composition of a captured sample. The sample was obtained with an explosively-sealed probe which had been developed at CAL. Because of the rapid cooling of the captured sample by the probe, it was anticipated that the temperature of the sample would be sufficiently low to result in the conversion of the captured NO to NO_2 . An attempt was made to infer the NO concentration of the free stream by measuring both the NO_2 concentration and the resultant O_2 deficiency in the sample. It was found that these measurements were limited by several considerations. Among these were chemisorption of NO_2 on the interior of the stainless-steel probe, and an apparent diffusive separation caused by the blunt-nosed probe which was used. These effects were eliminated by conditioning the probe through pretest exposure to NO_2 and by adding a conical nose piece to the probe. With these changes it was verified that NO was collected, but it was not possible in the present experiments to obtain a quantitative measurement of the NO_2 in the sample. This appeared to be the result of water vapor contamination which reacted with free NO_2 and O_2 to form HNO_3 . However, significant O_2 deficiencies were found which agreed fairly well with those expected.

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LIST OF SYMBOLS

- γ Specific heat ratio
- p' Pitot pressure
- a_* Stagnation speed of sound based on frozen stagnation temperature
- A_p^* Probe orifice area
- ρ' Stagnation density corresponding to the frozen stagnation temperature and the pitot pressure
- ρ Gas density
- P Gas pressure
- A_p Probe internal cross-sectional area
- L_p Cavity length
- T Gas temperature
- T_* Frozen stagnation temperature
- t Time
- \dot{q} Total heat transfer rate to the probe
- C_p Specific heat at constant pressure
- P_R Reservoir pressure
- T_R Reservoir temperature

I. INTRODUCTION

An explosively-actuated gas sampling probe shown schematically in Fig. 1 has been developed at CAL for the purpose of detecting the time of arrival of the hydrogen/air interface in the CAL 6-ft. Shock Tunnel. This work is described in detail in Ref. 1. In those experiments, blunt-nosed probes were mounted in the 6-ft. nozzle which, together with the probe, was evacuated in preparation for the firing of the shock tunnel which was operated in the reflected mode. When the flow was initiated, a detached shock wave formed in front of the probe which then filled at a rate that was proportional to the orifice area. At a predetermined instant, the explosively-driven ram, mounted through the rear of the probe, was fired, thereby driving the ram forward and sealing the collected sample inside the probe. The probe was then removed from the nozzle and the collected sample transferred to a gas chromatograph which was set up to analyze for O_2 , N_2 , Ar, and H_2 .

During the early experiments with air of Ref. 1, a persistent oxygen deficiency was found which increased with the reservoir temperature. Additional experiments, described in Refs. 1 and 2, were performed to determine the possible source of the oxygen loss. By a systematic variation of driver and driven gas combinations, interface combustion and heterogeneous reaction at the tube walls were eliminated as probable causes. In these experiments a significant O_2 deficiency occurred only when the driven gas included N_2 . This suggested the possibility that the probe was quenching the NO expected to be frozen in the free stream as a result of chemical nonequilibrium in the nozzle expansion. During cooling in the probe

the NO in the captured sample could react with excess oxygen to form NO_2 . This viewpoint was buttressed by the close agreement obtained between the measured O_2 deficiency and that predicted by calculating the nonequilibrium flow chemistry using the computer programs reported in Refs. 3 and 4, and assuming that all of the NO entering the probe was converted to NO_2 . Additional evidence was presented in Ref. 2 where sampling probe pressure records obtained in Ref. 1 were interpreted with the aid of a simplified gasdynamic analysis. On this basis, it appeared that the gas temperature in the cavity was much lower than the stagnation temperature of the gas. In this event, NO would be expected to convert to NO_2 within the framework of the chemical model considered herein.

In the conversion of N_2 and O_2 to NO_2 , one also would expect a deficiency in the N_2 concentration, but this was not found in Ref. 1. However, in those experiments the gas chromatographic analyses measured only the percentage composition and this concealed the N_2 deficiency due to both the small amount of N_2 consumed and the decrease in the total molar concentration due to formation of NO_2 .

The results reported in Refs. 1 and 2 and the theory presented herein suggest that it should be possible to infer certain features of the free-stream composition in a nonequilibrium air flow from the O_2 , N_2 , and NO_2 content of a collected sample. The present series of experiments were designed to explore this possibility.

In order to measure the deficiencies of both O_2 and N_2 by gas chromatography, a small amount of Ne was added to the test gas as an inert standard to which the concentrations of N_2 and O_2 in both the initial test gas and the collected sample could be compared. In addition, provision

was made to measure the NO_2 in the collected sample with a spectrophotometric method.

In Section II, simplified theoretical consideration is given to the probe gas dynamics and chemistry, and experimental pressure data for the internal probe flow are discussed. The calibration, sampling, and supplementary experiments are described in Section III.

II. GASDYNAMIC AND CHEMICAL BEHAVIOR

A schematic drawing and a photograph of a blunt probe of the type used in Ref. 1 is shown in Figs. 1 and 2, respectively. This probe is essentially a flat-faced stainless-steel cylinder with an external diameter of about 1-1/2" and an open orifice of 9/32" diameter centered on the probe face. The collected gas sample is drawn from the shock layer through the open orifice and then sealed inside the probe by firing the explosively-driven ram.

In some of the experiments reported herein, it was found desirable to add a conical nosepiece to the blunt probe. The nose cone is shown schematically in Fig. 3 and a photograph of the conically-tipped probe is shown in Fig. 2. A mounting plate was designed to bolt to the face of the blunt probe. The conical nose piece is then screwed onto the mounting plate.

It can be shown that a detached shock wave cannot exist for the conically-tipped probe during the filling period. Instead, it appears that a swallowed oblique shock system should exist in the entrance duct with a conical shock attached to the lip of the truncated-cone nose piece.

The following discussion of a simplified gasdynamic model for the filling period applies explicitly to the blunt probe only. However, this restriction enters in the expression given for the mass influx which is a constant in both cases. Consequently, the qualitative conclusions are applicable to both probes. In addition, the discussion of the chemical model which is presented does not depend on the shape of the probe.

A. SIMPLIFIED GASDYNAMIC MODEL

The detailed internal flow field within the probe during the filling period is, of course, complex and nonuniform. This is borne out by the experimental data for the internal pressure history to be discussed later in this section. Despite the complexity of the actual internal flow during filling, it is qualitatively useful to consider a very simplified model based on the following assumptions:

1. The gas in the probe during filling has negligible kinetic energy and has a time-varying thermodynamic state characterized by spatially-averaged values of pressure, density, and temperature related by the ideal gas law.
2. The filling orifice is choked at local sonic conditions.
3. The development time for establishment of quasi-steady filling is small compared to the filling period so that the mass of gas collected in the initial transient flow is a negligible fraction of the total collected mass.

With these assumptions, the mass influx to the blunt sampling probe can be written as a function of the specific heat ratio, effective frozen stagnation conditions, and the inlet area of the probe. The instantaneous space-averaged gas density in the probe is the product of the mass influx, which is a constant, and the time from flow initiation provided the initial mass in the probe and the nozzle starting time is negligible. Under the same assumptions, the space-averaged pressure can be obtained from an energy balance using the known mass influx. The following expressions are obtained for the pressure, density, and temperature, respectively:

$$P = \gamma \left(\frac{c}{\gamma+1} \right) P_0' \frac{A_p^*}{A_p} \cdot \frac{a_s t}{L_p} - \frac{(\gamma-1)}{A_p L_p} \int_0^t \dot{q} dt \quad (1)$$

$$\dot{q} = \left(\frac{c}{\gamma+1} \right)^{\frac{\gamma+1}{2(\gamma-1)}} P_0' \frac{A_p^*}{A_p} \cdot \left(\frac{a_s t}{L_p} \right) \quad (2)$$

$$T = \gamma T_0 - \frac{\dot{q}}{C_p A_p^*} \frac{a_s}{P_0'} \left(\frac{\gamma+1}{2} \right)^{\frac{\gamma+1}{2(\gamma-1)}} \quad (3)$$

In addition, Eqs. (1) and (3) can be combined to yield

$$T = \left(\frac{\gamma+1}{2} \right)^{\frac{\gamma+1}{2(\gamma-1)}} \frac{A_p}{A_p^*} \cdot \frac{T_0}{P_0'} \cdot \frac{L_p}{a_s} \cdot \frac{dP}{dt} \quad (4)$$

The notation is defined in the list of symbols. In particular, \dot{q} is the total rate of heat loss to the probe walls. Several conclusions can be drawn from Eqs. (1) to (4). Firstly, for known reservoir conditions and probe geometry, the gas temperature in the cavity can be inferred from Eq. (4) if the rate of pressure rise in the probe is known. Secondly, it is clear from Eq. (4) that a linear pressure rise implies that the gas temperature is constant during the filling period. It follows, then, from Eqs. (1) and (3) that this is only possible if \dot{q} is a constant.

The filling period ends when the explosive valve is fired and the probe is sealed. Then it can be shown that the temperature of the collected gas sample decays exponentially to that of the probe walls. For the present experiments, the decay time is of the order of 1 msec.

In the experiments reported in Ref. 1, pressure measurements were made using a dummy sampling probe with a side-mounted pressure transducer.

These pressure records displayed a very linear pressure-time behavior. Cavity temperatures several thousand degrees lower than the stagnation temperature can be inferred from these records with the aid of Eq. (4). As a consequence of the chemical analysis summarized in the following section and detailed in the Appendix, this result further supported the notion that the probe was behaving as a rapid-quench device serving to convert NO to NO_2 and suggested that a detailed analysis of the filling period could be performed within the framework of the model presented above with an empirically determined constant heat transfer rate.

Subsequent experiments performed in this program revealed that the pressure history recorded within the probe is strongly dependent on the position of the pressure sensor. This is illustrated in Fig. 4 where tracings of the dummy-probe internal pressure records for three different transducer positions are shown. The records labeled 1, 2, and 3 were obtained during three different tests at almost identical conditions. The first trace was obtained with a transducer mounted on the probe axis on the rear face of the cavity. This clearly indicates the highest pressure, about 8 times greater than that of trace 2 which is the output of a side-mounted transducer whose diaphragm face was about $1/4"$ off the probe axis. The third trace was obtained during a test in which the sampling probe was fired. At the instant of firing, the third transducer, which was side-mounted $7/16"$ off the probe axis, indicated a pressure about twice that obtained in trace 2.

These records suggest that a relatively high-speed flow exists along the centerline of the probe. This flow appears to stagnate nonisentropically on the rear wall and to recirculate along the sides of the cavity.

While the existence of a complex nonuniform flow within the cavity does not in itself prevent the definition of an instantaneous average state within the cavity, it does obscure the interpretation of calculations based on an average state and prevents the inference of a unique cavity temperature from cavity pressure measurements. For example, the temperatures deduced from the records of Fig. 4 with the aid of Eq. (7) range from about 500°K to 3500°K.

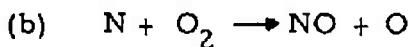
Nevertheless, the simple theory above does predict some of the qualitative features of the flow in that the pressure at each point did rise at nearly a constant rate. Also, it is clear from the results presented in the discussion of the experiments in Section III that quenching did occur which indicates that the sample was cooled rapidly. This is evident from the fact that oxygen deficiencies and an NO containing compound were observed. If the sample within the probe was initially at an average temperature greater than about 3000°K and the chemical reaction rates were comparable to the cooling rate, equilibrium would be maintained throughout the cooling process and the final composition of the captured sample would have been that of the original undissociated test air.

B. THEORETICAL SAMPLE CHEMISTRY

The purpose of this section is to summarize the expected dominant reaction mechanisms under conditions where the heat transfer to the probe is important. A complete discussion of the chemical model is given in Appendix A.

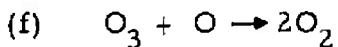
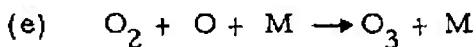
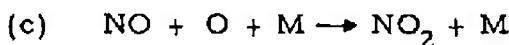
If the heat transfer to the walls of the probe is sufficiently high, the collected sample temperature will be low. This cooling effect has a strong influence on the chemical processes which occur within the probe.

For the reservoir conditions prevalent in these experiments, the gas entering the nozzle has approximately the following molar composition 76.1% N₂, 14.9% O₂, 6% NO, 3% O, and a much smaller amount of nitrogen atoms. Assuming an essentially frozen flow, all of these species should enter the probe with roughly these relative concentrations. The only reactions which are fast enough to compete with the filling process are



but the latter reaction is only important at cavity temperatures greater than about 3000°K. However, if the free-stream concentration of N atoms is much less than that of NO and O₂, these reactions will not significantly affect the gas composition.

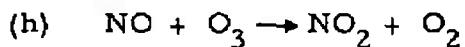
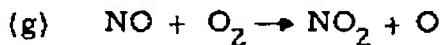
During the later stages of the filling period and after the probe is fired, the following reactions are important



The rates of all of these reactions decrease as the cavity temperature increases, and at cavity temperatures above 3000°K the reverse of reactions (c) and (d) would prevent significant free radical removal.

Later, during the final cooling stage, reactions (c) and (d) will be the dominant kinetic processes, while other reactions involving both the

initial species (N_2 , O_2 , O, NO, N) and the species formed within the probe (NO_2 , O_3) will contribute only slightly to the final composition; i. e.,



In summary, it can be seen that despite the diversity of reactions that can occur, the chemical processes lead to the conversion of NO to NO_2 and to the recombination of oxygen atoms, provided that the cavity temperature is below about $3000^{\circ}K$ and the nitrogen atom concentration is much less than that of NO.

III. DISCUSSION OF EXPERIMENTS

The experiments performed during this investigation fall into three categories. The first consists of routine calibration of the tunnel and chemical-analysis equipment. Chemical sampling experiments, which followed the completion of the calibrations, comprise the second set. Finally, during the sampling experiments, it was found necessary to perform several supplementary experiments in order to determine the source of discrepancies which were encountered.

A. CALIBRATION OF EXPERIMENTAL APPARATUS

The experiments discussed below were performed in the CAL Chemical Shock Tunnel which is described in Ref. 5. Briefly, it is a conventional shock tube coupled to a 30° conical nozzle. The nozzle has a throat diameter of 3/8" and is terminated with a 10" diameter at the dump tank. The tunnel was operated effectively tailored with a cold H₂ driver.

1. Nozzle Calibration

The nozzle calibration experiments consisted mainly of pitot pressure measurements designed to demonstrate the uniformity and to establish the duration of the test flow. Pitot and sampling probes were mounted on the end of a sting which extended through a mounting block suspended from the dump tank flange at the end of the nozzle by a system of four soft springs. Alignment was accomplished by adjusting the lengths of the block-to-spring connectors and counterbalancing the sting.

Lead zirconium titanate (PZT) crystal transducers, described in Ref. 6, were used in conjunction with commercial SLM transducers for the pitot and dummy sampling probe pressure measurements. The PZT transducers have a low acceleration sensitivity and have performed very satisfactorily with the mounting system used here.

A typical pitot pressure record is shown in Fig. 5. The pitot probe was mounted on the nozzle centerline about 7" upstream of the dump tank flange where the area ratio is about 480. Initially, the pressure rises for about 300 μ sec, which appears to be due to the nozzle starting process since this correlates with stagnation point heat transfer measurements. An additional check was made with a nitrogen test gas flow where the temperature was high enough so that the radiation from a small amount of sodium which had been added to the gas could be monitored. The nozzle starting time inferred from these measurements is consistent with that suggested by the pitot records.

The starting process is followed by a period of uniform flow which lasts from about 800 to 1400 μ sec, depending on the axial location of the pitot probe. The uniform flow is followed by a transient of about 300 μ sec, to a higher pressure plateau. The leading edge of this transient has been interpreted as the arrival of the interface. The sampling experiments which are described below suggest that this interpretation is essentially correct.

The results of three pitot pressure surveys across the nozzle at the 7" position using a three-pronged rake with flush-diaphragm transducers are shown in Fig. 6. The survey was made during three calibration experiments at the test condition selected on the basis of theoretical calculations of the

nonequilibrium flow chemistry. That particular test condition was chosen because it provides about the largest free-stream NO concentration which can be obtained. The resultant reservoir conditions were $P_R = 1200$ psia and $T_R = 3300^{\circ}\text{K}$, which result in a local Mach number of about 9 and unit Reynolds number of about $10^5/\text{ft}$ at the test position. The results shown in Fig. 6 indicate that the pitot pressure is uniform and reproducible at 5.0 psia to within $\pm 6\%$ in the 3-1/2" diameter core over which measurements were made at the axial location investigated (area ratio of 480). At this position, the nozzle diameter is about 8.2" and calculations presented in Ref. 6 indicate that the boundary layer displacement thickness should be less than 1/2". For given driver and driven gas pressures, the shock speed was reproducible to within $\pm 2\%$ and hence the desired reservoir conditions could be accurately reproduced.

2. Gas Analysis Methods

The gas chromatograph used is a Perkin-Elmer Vapor Fractometer Model 154B, which uses a heat-transfer-type sensing element. Separation of the gases was obtained by a one meter molecular sieve I column. A known constant volume of the sample to be analyzed was injected into a helium flow which carried it into the chromatograph unit. Peak height was taken as a measure of relative concentration and analysis of several samples from a known gas mixture showed that these results agreed to better than $\pm 2\%$.

The chromatograph as described provides a reliable analysis for O₂, N₂, and Ne. H₂ can also be detected, but little separation occurs between Ne and H₂ in the absorption column used and it is difficult to quantitatively determine these gases when both are present.

Gas chromatography is not a suitable technique for detecting NO_2 which was of particular interest in these experiments. Consequently, a spectrophotometric absorption-cell method was devised which makes use of interference filters having a band pass of 100 Å centered at 4280 Å. The NO_2 concentration was inferred from the amount of light absorbed over a 10 cm path length. Calibration was performed using known samples of NO_2 in N_2 . This gave results which agreed very closely with data obtained elsewhere (Ref. 7). The lower limit of detection of NO_2 was a partial pressure of ~ 1 mm NO_2 in the 10 cm path length cell. Neither of these analytical techniques would detect the presence of NO. However, the conversion of NO to NO_2 in the presence of excess O_2 is known to be rapid and would be complete within seconds after the experiment is completed.

B. EXPERIMENTAL PROCEDURE

Prior to each experiment, a known mixture of neon and air was prepared in a mixing tank for the test gas and two samples of this were taken for calibration purposes. Following the test, the sampling probe was removed from the nozzle and attached to the glass vacuum apparatus connected to the gas chromatography unit. Here the sample was divided into two approximately equal volumes, one of which was analyzed on the gas chromatograph while the other was examined spectrophotometrically for the presence of NO_2 .

All the experiments were conducted at a nominal reservoir pressure and temperature of approximately 80 atm and 3300°K, respectively. This reservoir state was found to be readily reproducible to within 2%.

The test gas was Matheson air which had the following quoted volumetric composition:

O ₂	=	20.85%
N ₂	=	79.15%
CO ₂	=	6 ppm
H ₂ O	=	3 ppm

C. RESULTS

The initial experiments disclosed two major difficulties: 1) there was a large neon deficiency in the collected sample, and 2) the observed deficiency in molecular oxygen was much smaller than anticipated. This is illustrated by the results of Table I for a typical test (test number 11). For this experiment, the blunt probe was mounted about 50% out on the radius at the axial position where the area ratio was about 480. The neon collected in the sample was about 1/3 the proper amount while the molecular oxygen collected was about 20% greater than anticipated (see theoretical predictions of Table I). Moreover, no NO₂ was detected in the sample.

1. Adsorption Investigation

In view of the above results, another set of experiments was performed which were designed to explore the possibility that the Ne deficiency and the lack of NO₂ were caused by adsorption. First, known amounts of Ne and air were stirred in the mixing tank and subsequently loaded into the driven tube of the shock tunnel at the same pressure used during the tests (260 mm Hg). After about 5 minutes, the usual elapsed time before the test

firings, a sample was withdrawn. The composition of this sample was compared to that of a mixing tank sample drawn prior to the filling of the driven tube. No Ne adsorption on the shock tube walls was indicated.

As a further check, a probe was fired in a bell jar containing the gas mixture of O₂, N₂, NO₂, and Ne expected to be found in the probe during the shock tunnel tests. Analyses of the Ne and NO₂ content of the captured sample indicated that essentially the correct composition was obtained. This result indicated that the firing of the probe did not cause a significant depletion of the Ne or NO₂.

Another experiment was performed to check on the adsorption of Ne and NO₂ on the interior surfaces of the sampling probe. The bell jar experiment could not be considered definitive in this respect because, prior to firing, the probe interior could have become conditioned by exposure to the gas mixture without significantly altering the gas composition in the bell jar. A sampling probe with a sealed orifice was evacuated and connected to a tank containing a known air/neon mixture. The probe was then filled with this mixture by opening and then immediately closing the interconnecting valve. The composition of this gas was analyzed after an elapsed time of about 20 minutes. No significant Ne adsorption was detected. This experiment was repeated with the glass sampling bottles used in the calibration experiments with the same results.

This last procedure was also performed with an air/NO₂ mixture. In this case it was found that a large NO₂ depletion occurred with probes which had not been previously exposed to NO₂. Measurements with the same probe made after NO₂ exposure indicated that the depletion was

decreased by the exposure even with prolonged evacuation between exposures. This suggested that the NO_2 adsorption is a chemisorption phenomenon and that therefore the probe could be conditioned so that useful measurements of captured NO_2 could still be obtained.

The careful measurements published in Ref. 8 indicate that this conclusion is correct. Those measurements are directly applicable to the sampling probe experiments because the data were obtained in the same pressure and temperature range. In particular, the data of Ref. 8 indicate that about 30 cm^2 of clean stainless steel surface area would be required to completely chemisorb the amount of NO_2 expected in our experiments. This area is comparable to the geometric internal area of the sampling probe.

The check experiments described above provided a possible explanation for the absence of NO_2 in the previous sampling experiments. As a result, in the subsequent experiments, the probes were conditioned and checked for NO_2 chemisorption before each test. However, the check experiments did not reveal any possible mechanism which would explain the apparent Ne loss.

2. Investigation of Diffusive Effects

The results of the adsorption check experiments suggested that the Ne loss was a real effect and further examination of the problem suggested that it might be caused by diffusive separation in some part of the flow. The most likely possibility for these test conditions is the blunt-probe separation effect described in Ref. 9. Although the theoretical understanding of the separation mechanism seems to be limited at present, experiments such as those of Refs. 9 - 12 clearly indicate that a detached bow wave is intimately connected

with the effect. Significant diffusive separation in the nozzle does not appear to be possible on the basis of the results of Ref. 13.

In an effort to prevent possible flow-field diffusion effects, a conical nose piece was designed to eliminate the detached shock wave. The resultant nose cone is shown schematically in Fig. 3 and a probe with the nose cone attached is shown in Fig. 2.

Calculations were performed which indicated that a detached shock wave cannot exist for this configuration during the filling period of the probe. Instead, it appears that a swallowed oblique shock system should exist in the entrance duct with a conical shock attached to the lip of the truncated-cone nose piece. As a result, shock layer diffusion effects should have been eliminated by this modification.

A series of experiments was made at various axial stations in the nozzle using the conical probe. The experiments identified as tests 17 and 18 in Table I summarize these results. In both of these experiments, the sampling probe was mounted on the nozzle centerline at an area ratio of about 335. In both samples, the chemical composition is in agreement to better than $\pm 1\%$ which is within the experimental error. The results of these two tests are notable not only for their consistency, but also because the indicated Ne deficiency is at most only a few percent. Leak-rate checks have indicated that this small deficiency is probably only an apparent one caused by an air leak into the probe. The leak rate is very small but is important because of the small gas sample which is collected and the relatively long time which elapses before the probe can be removed from the tunnel for analysis.

Again, NO_2 was not detected even though an O_2 deficiency of about 17% was obtained. While this deficiency is somewhat smaller than the predicted value (obtained from reservoir conditions and using the CAL non-equilibrium flow computer program, Ref. 3) given at the bottom of Table I, it is considerably larger than found in the off-axis blunt-nosed probe experiments (see test 11).

In the next experiment, test 19, a blunt-nosed probe was used under the same conditions as in tests 17 and 18. In this experiment, part of the collected sample was analyzed with a modified Consolidated Electrodynamics 21-613 Mass Spectrometer in order to provide a check on the gas chromatograph and absorption cell analysis. The gas chromatograph indicated that there was an 8% Ne deficiency in this sample and once again no NO_2 was detected. While this Neon deficiency is much smaller than that obtained in the early, off-axis experiments, it is significant since essentially no Ne deficiency was found with the conically-tipped probe. In addition, the O_2 concentration in this sample was about 4% lower than that in the sample obtained under similar conditions with the conically-tipped probe. This implies that the O_2 deficiency is about 20% greater than in tests 17 and 18. This deficiency agrees quite well with the theoretical expectations as given in Table I.

It should be noted that the differences in composition obtained with the blunt and conically-tipped probes cannot be consistently explained in terms of a difference in the leak rates. For example, if the leak into the conically-tipped probes were larger than for the blunt probe of test 19, then the O_2 and Ne contents relative to N_2 would be smaller and larger, respectively, in test 19 than in tests 17 and 18. The results summarized in Table I indicate that while the O_2 content in test 19 is smaller, the Ne content

is not larger. Consequently, the differences between the two sets of experiments cannot be explained on the basis of different leaks into the probes. This conclusion also holds for the discrepancies between the gas chromatograph and mass spectrograph results for test 19 discussed below.

3. Effect of Water Vapor Contamination

The mass spectrographic analysis agreed with that from the gas chromatograph to within about 10%, which reflects the accuracy of the available mass spectrograph. Therefore, it was not possible to confirm the magnitude of the Ne deficiency. However, the mass spectrographic results did clarify the apparent lack of NO_2 indicated in this and the other experiments by the absorption cell method. It appears that there was a significant amount of some nitrogen-oxygen compound in the sample, but this compound did not show the characteristics of free NO_2 . This was determined by calibrating the mass spectrograph with pure NO_2 . The resulting mass spectra shown in Table II contains three dominant peaks at masses 30, 46, and 16, corresponding to NO^+ , NO_2^+ , and O^+ , with relative peak heights of 100, 28.2, and 18.1 respectively. Thus NO_2 is mostly dissociated as it is ionized in the mass spectrograph.

Since the gas density in the mass spectrograph is extremely low during and after ionization, collision processes can be neglected. Consequently, the addition of another gas to the NO_2 cannot alter the peak height ratios given above as long as the added gas contains no ionized products corresponding to the above mass numbers. In the particular case of air, the mass spectra contains no peaks at masses 30 and 46. Therefore, the sample collected in the nozzle if it contains free NO_2 ,

should have mass 30 and mass 46 peak heights which are in the ratio of 100 to $28.1 = 3.56$. Instead, a peak height ratio of 130 was obtained. Clearly then, although a significant amount of some nitrogen-oxygen compound was present in the sample, it could not have been free NO_2 .

Small amounts of H_2O and H_2 were detected in the collected sample. Both gases appeared in quantities greater than could be accounted for by background contamination in the mass spectrometer or by contamination in the test air being used. This indicated that either a part of the interface had been collected or that the collected sample had picked up these impurities from some other source. The presence of H_2O suggested that HNO_3 might be the end product of quenched NO in this case. To check this, a wet air and NO_2 sample was analyzed. This sample had essentially the same characteristics as the collected sample (see Table II). From this, it appears that NO_2 was not observed with the absorption cell because of H_2O contamination. It was not possible to obtain a quantitative measure of the NO_2 originally present using the mass spectrograph because of the reaction of HNO_3 with the brass piping and fittings used in the instrument.

It should be pointed out here that the use of Ne to detect the nitrogen deficiency was unsuccessful. The experimental results obtained where there was little ambiguity from the Ne deficiency showed that the Ne/N_2 ratio in the sample was never greater than that for the test gas, and in any case the small changes in nitrogen concentration corresponding to the observed O_2 deficiencies would be within the experimental accuracy reported herein.

IV. CONCLUDING REMARKS

The results of this investigation support the concept that a sampling probe of the type discussed herein can be developed as a rapid-quench device to provide quantitative data on free-stream air composition. Although there were several inherent difficulties, the persistent oxygen deficiency observed in the present experiments is most readily interpreted as due to the quenching of NO within the probe.

The present results suggest that probe geometry and flow angularity have an influence on the chemical composition of the collected sample. For example, in early off-axis tests of a blunt-nosed probe where the probe is effectively at an angle of attack because of source-flow effects in the conical nozzle, the amount of Ne collected increases with orifice diameter. In addition, the amount of O₂ decreases with respect to N₂ when the effective blunt-probe angle of attack is decreased. When the bow shock wave is eliminated, as it is with the conical adapter, essentially the correct amount of Ne relative to N₂ is collected. The O₂ deficiency obtained with the conically-tipped probe is less than that for the blunt-nosed probe operated on axis but more than when the latter is operated off axis. Thus it appears that probe geometry and flow angularity can affect the O₂ deficiency.

In these experiments, NO₂ was never detected with the absorption-cell method even though it should have been easily detectable. This result is consistent with the mass spectrographic measurements which clearly indicate that a nitrogen-oxygen compound other than NO₂ is present in the sample. All the evidence obtained thus far suggests that as NO is quenched, NO₂ is formed but it combines with H₂O to form HNO₃. Combustion at the

interface is a likely source of the H_2O .* However, this possibility would have to be checked in any future work directed toward the measurement of NO_2 with this technique. Chemisorption of NO_2 on the interior of the stainless steel probe was also a problem, but this was eliminated by conditioning the probe through prior exposure to NO_2 .

Further development of this diagnostic technique would entail solutions to the above mentioned problems. It would also be of interest in further studies to evaluate the use of metal mesh (e.g., steel wool) within the probe to enhance the quenching process and provide more uniform conditions within the cavity.

* It is interesting to note that the amount of H_2O collected greatly exceeded that of H_2 . This suggests a rather extended diffusive penetration of H_2 into the hot test air which then completely oxidized the H_2 .

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TABLE I
SUMMARY OF SAMPLING PROBE EXPERIMENTS

TEST IDENTIFICATION	PRE-TEST COMPOSITION			COLLECTED SAMPLE COMPOSITION			(O ₂ /N ₂) COLLECTED	(N ₂ /O ₂) COLLECTED	(O ₂ /N ₂) COLLECTED	COMMENTS	
	R ₂ /O ₂	N ₂ /N ₂	O ₂ /N ₂	N ₂ /O ₂	R ₂ /N ₂	O ₂ /N ₂	(O ₂ /N ₂) PRETEST	(N ₂ /O ₂) PRETEST	(O ₂ /N ₂) PRETEST		
11	3.79	26.4	6.98	4.09	72.4	17.6	No	0.926	0.365	2.53	a) BLUNT PROBE MOUNTED ABOUT 50S OUT ON NOZZLE RADIUS AT AREA RATIO OF 480. b) LARGE APPARENT N ₂ DEFICIENCY BUT SMALL O ₂ DEFICIENCY. c) PROBE WAS NOT CONDITIONED FOR RD ₂ CHEMISORPTION.
17	3.79	25.30	6.68	4.56	25.6	5.54	No	0.830	0.880	0.845	a) CONICALLY-TIPPED PROBE PLACED ON AXIS AT AREA RATIO OF 335. b) CONDITIONED PROBE. c) ALTHOUGH A SLIGHT N ₂ DEFICIENCY IS INDICATED, LEAK CHECKS INDICATE THAT THE N ₂ /N ₂ RATIO SHOULD BE CORRECTED UPWARD BY ABOUT 3% FOR THE ELAPSED TIME IN THESE EXPERIMENTS. THEREFORE VIRTUALLY ALL OF THE N ₂ WAS COLLECTED.
18	3.79	25.30	6.68	4.58	25.6	5.59	No	0.828	0.890	0.837	a) REPEAT OF TEST 17 TO CHECK ON REPEATABILITY. b) AGREEMENT IS WITHIN ABOUT $\pm 1\%$.
19	3.79	25.30	6.68	1) 4.75 27.5 2) 5.39 31.1	5.79	No	SEE COMMENT	0.796 0.703	0.919 0.815	0.867 0.865	a) REPEAT OF TESTS 17 AND 18 BUT CONICAL NOSE PIECE WAS REMOVED TO ASSESS AFFECT OF PROBE BLUNTNESST. b) ANALYSIS #1 IS BASED ON CHROMATOGRAPH AND ABSORPTION CELL MEASUREMENTS WHILE #2 ARE RESULTS FROM A MASS SPECTROGRAPH. c) THESE RESULTS ARE SIGNIFICANTLY DIFFERENT FROM THOSE OF PREVIOUS EXPERIMENTS. d) MASS SPEC AND GAS CHROMATOGRAPH RESULTS ARE IN QUALITATIVE AGREEMENT BUT DIFFER BY AS MUCH AS 12.5%. e) MASS SPEC RESULTS REVEALED THAT AN N ₂ O ₂ COMPOUND WAS PRESENT IN THE GAS BUT IT WAS NOT FREE NO ₂ . SOME N ₂ AND H ₂ O WAS FOUND ALSO (SEE TABLE II).
THEORY				0.778	1.025	0.751					

TABLE II
MASS SPECTRA SUMMARY FOR TEST 19
(NUMBERS REPRESENT RELATIVE PEAK HEIGHTS OF MASS SPECTRA)

MASS	"PURE" NO ₂	SHOCK TUBE SAMPLE	ROOM AIR	ROOM AIR +5% NO ₂
2	-	0.05	-	-
4	-	-	-	-
14	8.6	8.0	9.3	6.4
14.5	-	-	0.01	0.02
15	1.4	-	0.01	0.06
16	18.1	1.9	2.7	2.1
17	2.1	0.21	0.11	0.2
18	2.0	0.75	0.43	0.3
20	-	1.0	0.48	0.3
22	-	0.09	-	-
28	4.9	100.0	100	100
29		0.49	0.71	0.66
30	100	2.7	0.01	1.6
31	0.5	-	-	-
32	0.97	14.2	20.6	16.5
34	-	0.07	0.08	0.07
40	0.44	2.6	2.8	2.1
41	-	0.02	0.006	
42	-	0.02	0.002	0.006
43	-	0.04	0.008	0.02
44	7.5	0.27	0.08	0.12
45	-	0.07	-	0.02
46	28.2	0.02	-	-
47	0.41	-	-	0.03
48	1.4	0.02	-	-
64	2.7	-	-	-

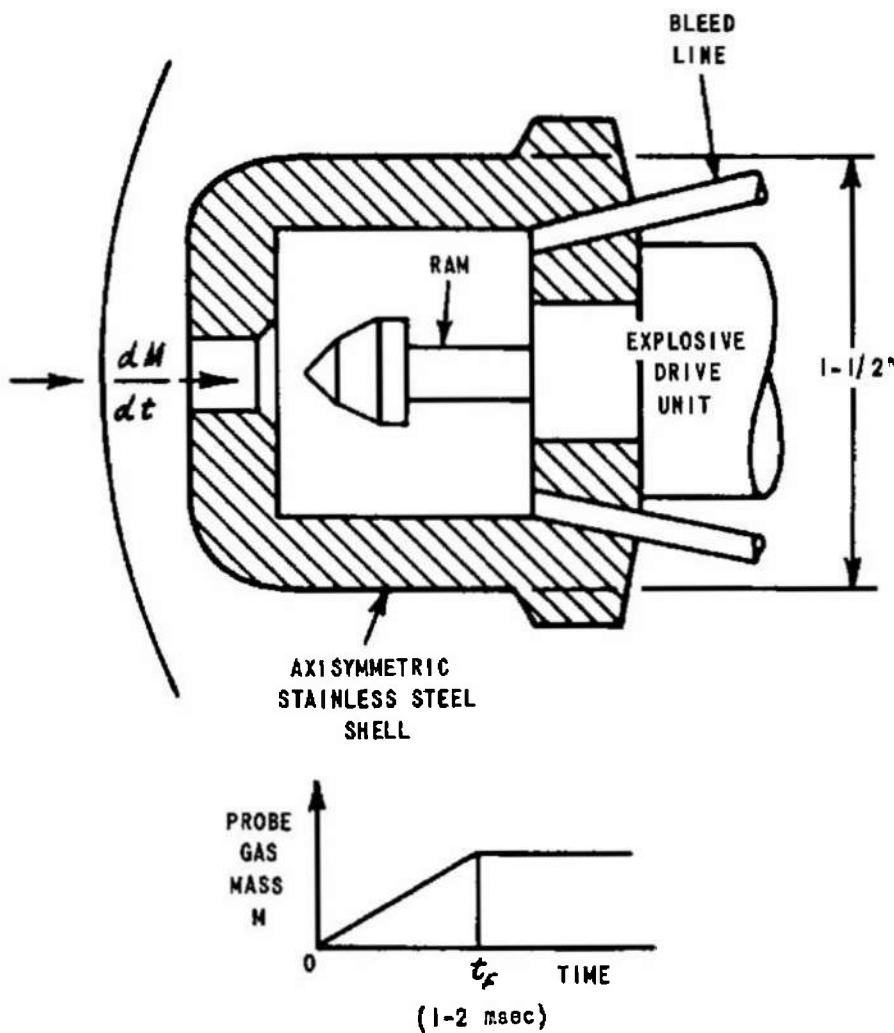


Figure 1 SCHEMATIC DIAGRAM OF BASIC SAMPLING PROBE

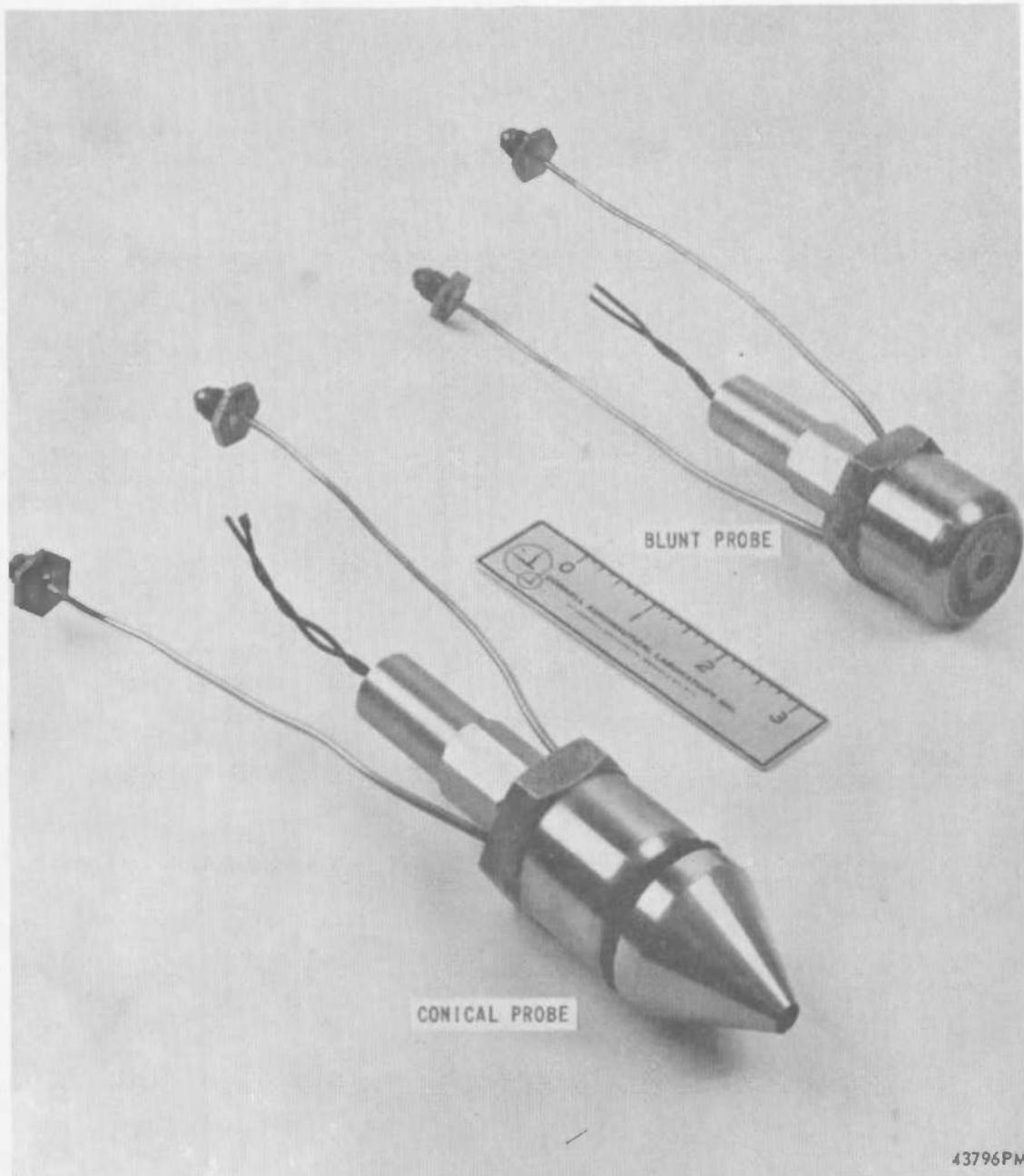


Figure 2 BLUNT AND CONICAL GAS SAMPLING PROBES

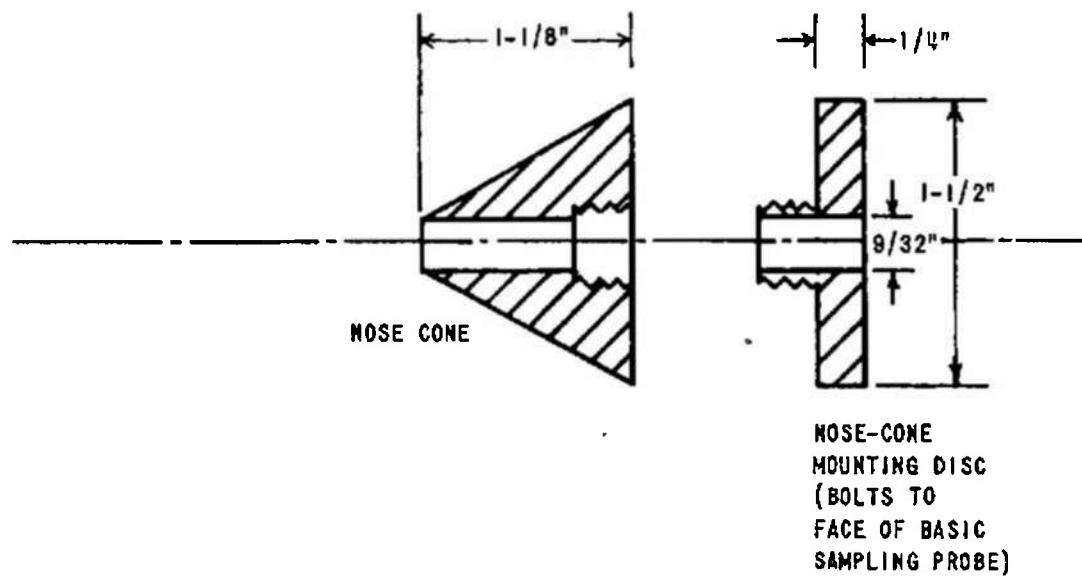
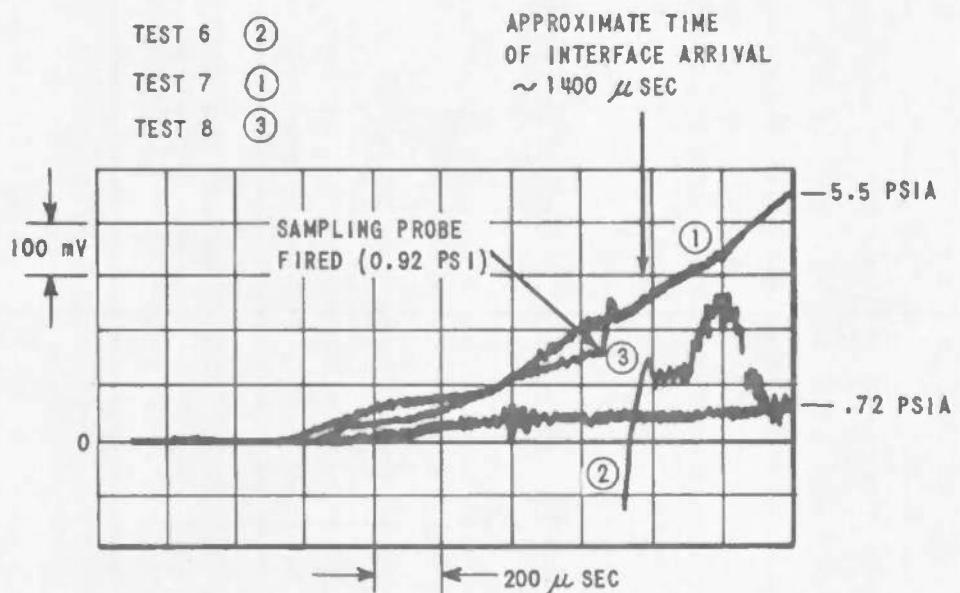
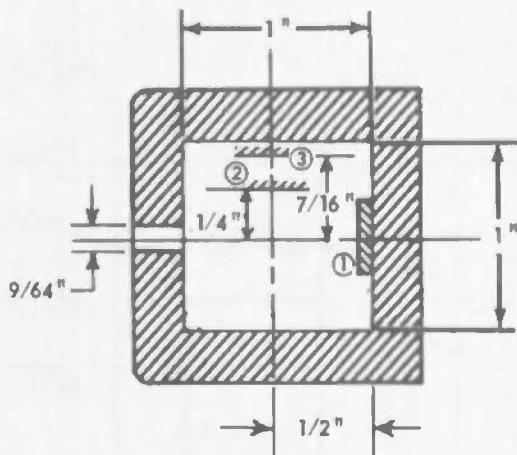


Figure 3 SCHEMATIC OF NOSE CONE MODIFICATION OF BASIC SAMPLING PROBE



(a) PRESSURE HISTORIES DURING FILLING OF DUMMY PROBE



(b) PRESSURE TRANSDUCER DIAPHRAGM LOCATIONS IN DUMMY SAMPLING PROBE

Figure 4 SUMMARY OF INTERNAL PRESSURE MEASUREMENTS

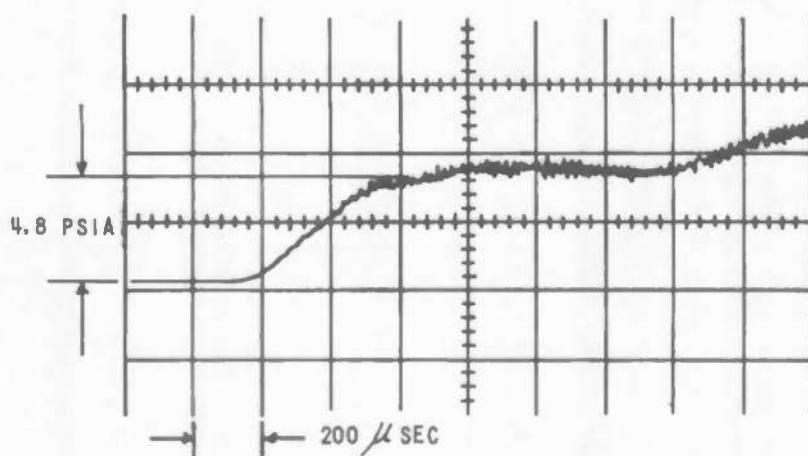
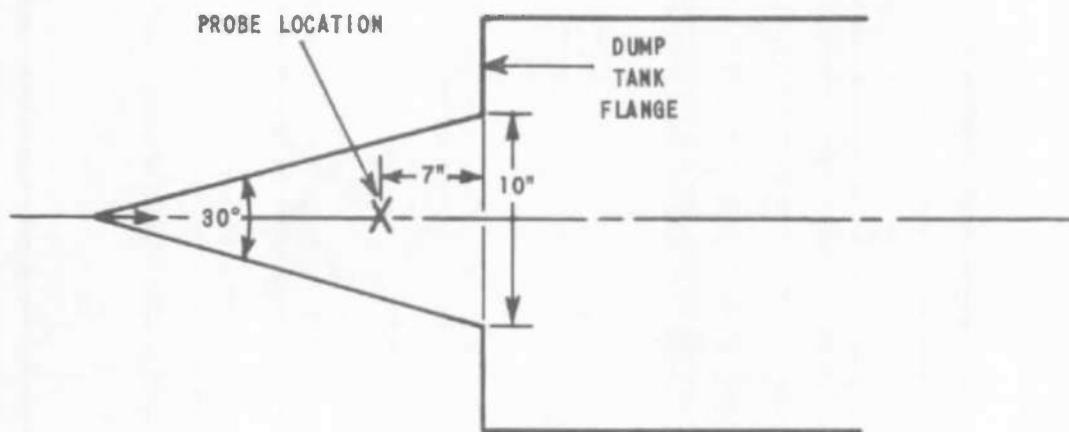


Figure 5 TYPICAL PITOT RECORD

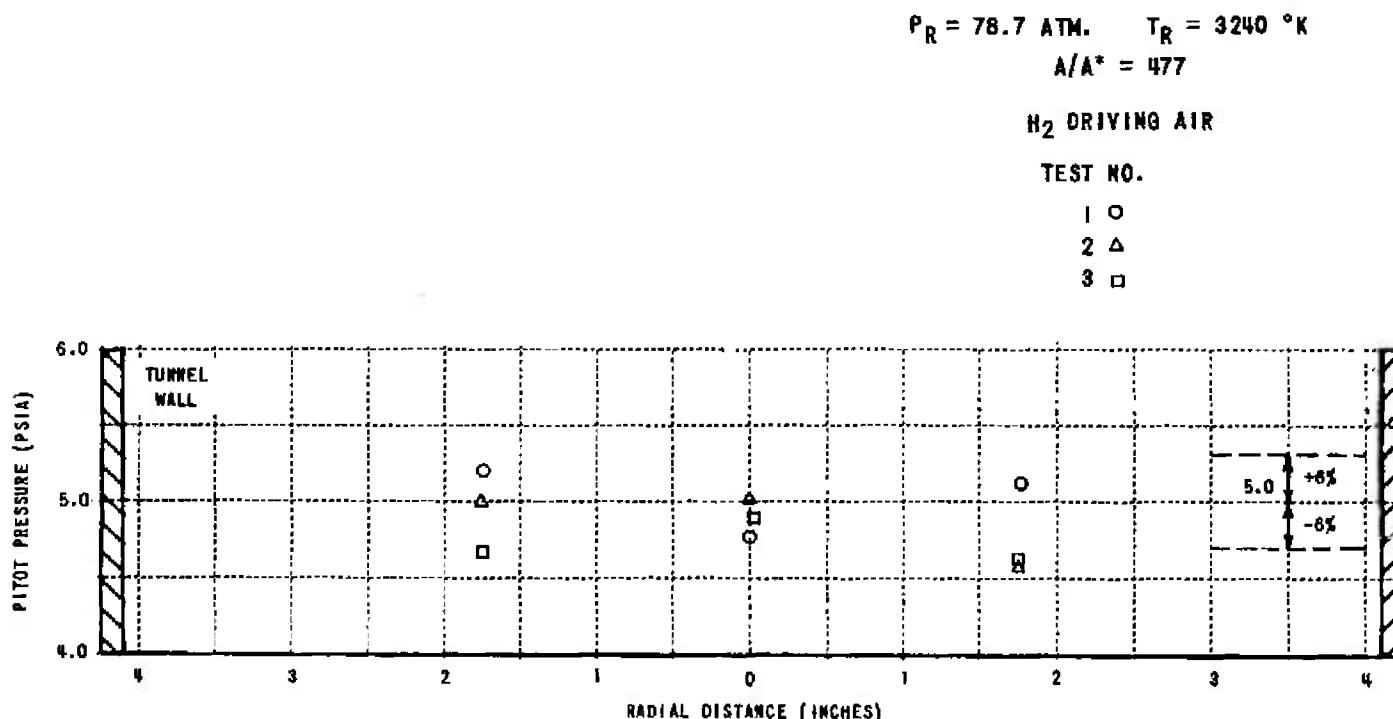


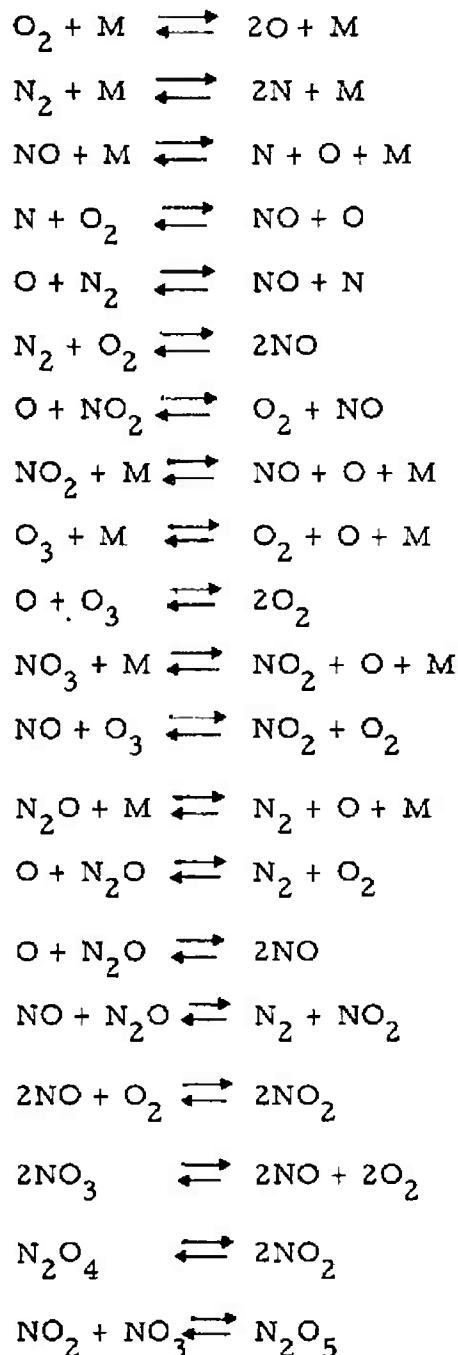
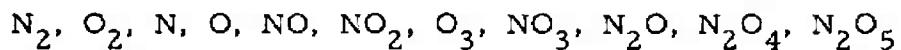
Figure 6 PITOT PRESSURE SURVEY RESULTS

**APPENDIX A
DISCUSSION OF THE THEORETICAL REACTION MECHANISMS**

The purpose of the following analysis is to find the probable important reactions and to establish the conditions under which an explosively actuated, gas sampling probe might theoretically be used as a diagnostic tool for non-equilibrium air flows. In the discussion below, the basic principle of operation of the probe is reviewed and a discussion of the theoretical model is given along with the conclusions which have been drawn.

In a nozzle flow, significant quantities of N, O, and NO may be frozen out. If the gas is collected at a low temperature, many of the reactions required to regain equilibrium at its initial composition will proceed so slowly that a sample analyzed after an experiment may possess a composition significantly different from that of ordinary air. This is the basis for the use of the sampling probe as a diagnostic for free-stream NO. This is possible provided that substantially all of the ambient NO is converted to a stable species, such as NO_2 , without the production of significant additional amounts of NO. In this event, the free-stream NO concentration could be inferred from the measured NO_2 concentration. The purpose of this Appendix is to examine the conditions for which this procedure may be valid.

In this connection, a chemical model for the collected sample consisting of the following 11 species and 20 gas-phase reactions has been examined:



Heterogeneous reactions have not been considered.

The rate data used in the analysis were taken from Ref. 14 for all except the last two reactions. It appears that these reactions can be ignored because of the low probe pressures at which these experiments are performed. The composition of the gas entering the probe has been determined over a range of reservoir conditions with the aid of CAL machine programs for the nozzle flow and the flow behind the bow shock wave. (Refs. 3 and 4).

Barring diffusion, the results of the analysis indicate that there are three conditions which limit the usefulness of the probe as an NO diagnostic. First, the shock layer must be nearly frozen with respect to NO. Second, the local temperature of the gas in the probe must not greatly exceed 3000°K. Finally, a significant N atom concentration must be avoided while the level of the O atom concentration does not appear to be critical.

The first condition is obvious while the second and third are not. However, the reasons for these restrictions can be understood by determining the dominant reactions and examining the resulting effect on the various species.

For the purpose of theoretical chemical analysis, it is convenient to divide the collection process into three distinct phases. The first is the loading phase in which some of the test gas flows through the bow shock of the probe and into the probe cavity. Because of cooling losses to the probe, the gas temperature in the cavity may be relatively low. At some predetermined time (usually about a millisecond after the flow is established), the probe is sealed by an explosively-driven plug. This signals the beginning of phase 2 which is characterized by a constant density and a more-or-less exponential temperature decay to room temperature that is accomplished in about 1 millisecond or less. In the third phase, the gas remains at room

temperature and constant density up to the time when the composition of the sample is analyzed.

During the loading phase, a reaction will be important only if it can change the concentration of a particular species at a rate comparable to its influx. Naturally, the cavity temperature plays an important role in determining the reaction mechanism during loading. However, as a result of the dummy probe pressure measurements described in Section II, there does not appear to be any way in which a meaningful representative cavity temperature can be estimated at the present time. However, the characteristic cooling time for the cavity is about the same order as the characteristic energy influx time and therefore one might expect the cavity to be reasonably cold.

When the local cavity temperature exceeds about 3000°K, NO removing reactions within the cavity may become important. For example, the following reaction becomes important at about 3500°K.



In this case the free stream NO could not definitely be inferred from the measured NO_2 concentration.

When the cavity temperature does not greatly exceed 3000°K, it appears that for the present probe geometry there is a broad range of reservoir conditions for which only three sets of reactions need be considered. In particular, the reaction



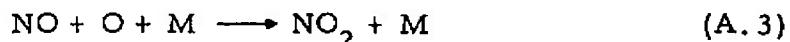
is extremely fast. In fact, during most of the filling period this reaction removes N at a rate that is more than an order of magnitude faster than the rate that N enters the cavity. As a result, some of the NO entering the probe will be converted almost instantly into N_2 rather than NO_2 . Clearly then, the concentration of N must be small compared to that of NO if this type of probe is to be used as an NO diagnostic. It should be pointed out that the equilibrium constant for this reaction is so large that all of the N (or NO, whichever is smaller) is essentially consumed.

If the cavity temperature rises above $3000^{\circ}K$, the following N-consuming reaction becomes important.



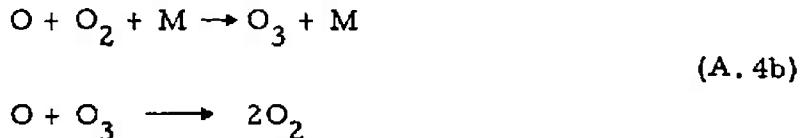
It can be seen that, in general, this reaction will also limit the usefulness of the probe when the N concentration is significant.

The second type of reaction which must be considered during the filling period, namely



is considerably slower than the exchange reactions above and as a result need only be considered when the amount of NO exceeds the amount of N since this reaction will lag behind reaction (A. 2a). In the case of reaction (A. 3), NO is converted to NO_2 by reaction with O, and as a result the presence of O does not limit the use of the probe as an NO diagnostic. The equilibrium constant for this reaction lies considerably in favor of NO_2 formation.

The third reaction set which may be important consists of competing O recombination paths which are usually about an order of magnitude slower than the NO₂ formation reaction (A. 3).



Whether reactions (A. 4a) or (A. 4b) dominate or are equally important depends on the particular case being considered. At high cavity temperatures (3000°K or more) the ozone reactions can be ignored and the reverse of reaction (A. 4a) may be important, depending on whether the O₂ in the shock layer flow is under- or over-dissociated with respect to conditions in the cavity. Consequently for a hot cavity, the reaction



must also be considered.

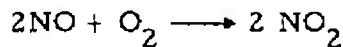
It is important to realize that when the cavity is cold, reactions (A. 4a) and (A. 4b) are usually important only if NO has been substantially depleted by reactions (A. 2a) and (A. 3) and significant O still remains after these reactions go to completion. On the other hand, if N and O are consumed by reactions (A. 2) and (A. 3) and a significant amount of NO remains, then there appear to be no reactions involving NO which are fast enough to compete with the influx of NO during the filling period.

During the temperature decay period following probe closure, a reaction will be important if its characteristic time is comparable with the temperature decay time. For the present probe geometry, the decay time is about one millisecond, which is about the same as the filling time. Consequently, the same reactions which are important during filling will be important during this period with the exception of the exchange reactions (A. 2a) and (A. 2b) which go to completion during the loading period.

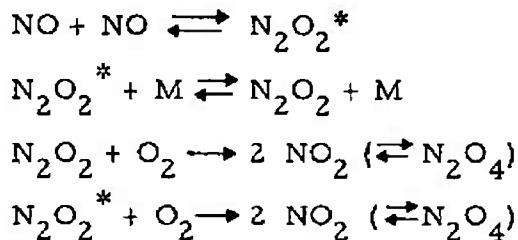
The chemical processes which occur after the cavity temperature falls to room temperature depend on the reactants which are still present. Briefly, any NO that remains is converted to NO_2 in this reaction model by reaction (3) and the following reaction*



* The actual mechanism by which NO is converted to NO_2 in the presence of O_2 is not known. However, recent work, Ref. 15, suggests that the correct mechanism is neither



nor that above. Instead, the dimer of NO may be involved. In Ref. 15 the following mechanism is suggested:



where N_2O_2^* is an excited state of N_2O_2 . Regardless of the proper mechanism, the basic conclusion that virtually all of the NO remaining after the first two phases will convert to NO_2 should not be affected.

Any O that remains combines to form O_2 and O_3 according to reactions (A. 4a) and (A. 4b). In cases where the NO and O_3 concentrations become large, the following reaction may also be important



The foregoing is summarized in the main text which outlines the expected important reactions during each phase of the probe operation. Only the cases for which the NO concentration is greater than the N concentration and the cavity temperature is $3000^{\circ}K$ or less are considered since these are the only cases in which the probe could be used as a diagnostic tool for NO. In the case where the N concentration is insignificant, the ultimate N_2 concentration in the sample will be that of the free stream. The composition of the remaining species (O_2 , NO_2 , O_3 , O, and NO) will be determined by the equilibrium produced by reactions c, d, e, f, g, and h listed in Section II. However, the equilibrium constants are so large for these reactions that it should be a good approximation to assume that the NO_2 concentration equals the free stream NO concentration. The O_2 concentration can then be calculated from simple stoichiometric considerations.

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY (Corporate author) Cornell Aeronautical Laboratory, Inc. Buffalo, New York 14221	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED
	2b. GROUP N/A

3 REPORT TITLEINVESTIGATION OF A RAPID-QUENCH SAMPLING PROBE FOR
NONEQUILIBRIUM AIR FLOWS**4 DESCRIPTIVE NOTES (Type of report and inclusive dates)**

Interim Report; March 1, 1965, through July 1, 1966

5 AUTHOR(S) (Last name, first name, initial)

Stoddard, F. J. and Watt, W. S., Cornell Aeronautical Laboratory, Inc.

6. REPORT DATE March 1967	7a. TOTAL NO. OF PAGES 48	7b. NO. OF REFS 15
8a. CONTRACT OR GRANT NO. AF 40(600)-1093	9a. ORIGINATOR'S REPORT NUMBER(S) AEDC-TR-67-65	
b. PROJECT NO. 8951	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) AG-1905-A-1	
c. Program Element 61405014		
d. Task 895106		

10. AVAILABILITY/LIMITATION NOTICES

Distribution of this document is unlimited.

11. SUPPLEMENTARY NOTES Available in DDC	12. SPONSORING MILITARY ACTIVITY Arnold Engineering Development Center Air Force Systems Command Arnold Air Force Station, Tennessee
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13 ABSTRACT

Shock tunnel experiments in air are reported which basically were designed to determine the free-stream composition from the gaseous composition of a captured sample. The sample was obtained with an explosively-sealed probe which had been developed at CAL. Because of the rapid cooling of the captured sample by the probe, it was anticipated that the temperature of the sample would be sufficiently low to result in the conversion of the captured NO to NO₂. An attempt was made to infer the NO concentration of the free stream by measuring both the NO₂ concentration and the resultant O₂ deficiency in the sample. It was found that these measurements were limited by several considerations. Among these were chemisorption of NO₂ on the interior of the stainless-steel probe, and an apparent diffusive separation caused by the blunt-nosed probe which was used. These effects were eliminated by conditioning the probe through pretest exposure to NO₂ and by adding a conical nose piece to the probe. With these changes it was verified that NO was collected, but it was not possible in the present experiments to obtain a quantitative measurement of the NO₂ in the sample. This appeared to be the result of water vapor contamination which reacted with free NO₂ and O₂ to form HNO₃. However, significant O₂ deficiencies were found which agreed fairly well with those expected.

Security Classification

14

KEY WORDS

rapid-quench sampling
 probes
 nonequilibrium airflows

LINK A		LINK B		LINK C	
ROLE	WT	ROLE	WT	ROLE	WT

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